



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP91/00274 <b>(22) International Filing Date:</b> 13 February 1991 (13.02.91) <b>(30) Priority data:</b> 9004161.7 23 February 1990 (23.02.90) GB <b>(71) Applicant (for all designated States except US):</b> MERCK PATENT GESELLSCHAFT MIT BESCHRÄNKTER HAFTUNG[DE/DE]; Frankfurter Str. 250, D-6100 Darmstadt (DE). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> SAGE, Ian, Charles [GB/GB]; 58 Wentworth Drive, Broadstone; Poole, Dorset BH12 4NN (GB). BAILEY, Jacqueline, Dawn [GB/GB]; 65 Martin Close, Creekmoor, Poole, Dorset BH12 4NN (GB). DAVIES, Thomas, Alan [GB/GB]; 23 Cooke Road, Parkstone, Poole, Dorset BH12 4NN (GB).		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> COLOURANT  <b>(57) Abstract</b>  The invention relates to a colourant based on platelet-shaped substances optionally coated with one or more metal oxides, which contains an iridescent liquid crystalline medium and which can be used for colouring paints, plastics, fibers, glasses, cosmetics and printing inks or as dye-stuff in hair colouring agents.		

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## Colourant

The invention relates to a colourant based on platelet-shaped substances optionally coated with one or more metal oxides, characterized in that it contains a chiral iridescent liquid crystalline medium.

There is a great need for colourants, particularly for cosmetic use which are free from separation, also good at spreading, application feel and pigment dispersibility, and moreover, excellent in their moisture-retention ability.

At present, for make-up cosmetics such as foundations, eye shadows, cheek rouges and other cosmetics, powder type colourants are widely employed because of their convenience.

However, these powder type cosmetics have disadvantages that they become dry or powdery, because the powder contents are high. In order to solve these disadvantages, a variety of oil type cosmetics have been designed and actually appeared on the market. Conventional oil type cosmetics have attempted to realize the application feel, usability and product stability which suit the application purpose by dispersing and mixing powders such as filler pigments, coloring pigments etc. in solid or semi-solid oil-based starting materials and changing their compositional ratios. Although the powderiness and dryness are somewhat reduced by the effects of the oily ingredients, these oil type cosmetics had a disadvantage that they are sticky because

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of their high oil contents. If therefore, in order to reduce this stickiness, for example, a semi-solid component such as wax etc. is increased, although the stickiness is improved, spreading becomes more difficult, and in  
5 conventional oil type coloured cosmetics, compositions which are fully satisfactory in both application feel and usability have not yet been obtained.

On the other hand, as a means to solve such problems as the above-described stickiness etc., it has been proposed  
10 to incorporate a gelling agent. As the gelling agent, there have been used natural or synthetic polymers, surfactants, inorganic clay minerals etc. Japanese Laid-open Patent Application No. 76543/1985 discloses an example where an oily component is incorporated in a lipophilic fatty acid  
15 ester and a starch hydrolysate saturated fatty acid ester, Japanese Laid-open Patent Application No. 56115/1986 discloses an example which contains an organically modified montmorillonite clay and a dextrin fatty acid ester and/or a lyophilic sugar fatty acid ester, and Japanese Laid-open  
20 Patent Application No. 67514/1984 discloses an example which contains a polyalcohol and a resin, but in every case, the amount of the gelling agent incorporated was great, therefore, when the gel strength was enhanced, there were problems, for example, spreading was difficult and it became  
25 sticky. Further, for those compositions using organic solvents, there is a problem concerning safety.

Further, users of oil type cosmetics require a moist feeling on the skin, but with the clogging effect due to the oil component in conventional oil-based coloured cosmetics, it is impossible to impart such a moist feeling to  
30 the skin, and thus it can hardly be said that satisfactory effects have been achieved for use during dry weather and on dry skin.

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On the other hand, in order to impart a moisture-retaining effect, an attempt to incorporate a humectant has been tried, but the conventionally employed humectants, for example, glycerin, propylene glycol, etc. are difficult to  
5 incorporate into oily component systems, and significant effects have not been obtained.

Furthermore, the Swiss Patent Application CH 491 533 discloses that micro-encapsulated cholesteric liquid crystals can be used in aqueous suspension as colourants for decorative appli-  
10 cations.

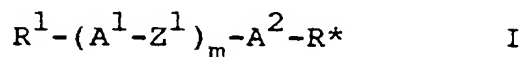
The present inventors have discovered that colourants based on platelet shaped substances optionally coated with one or more metal oxides containing a chiral iridescent liquid crystalline medium solve the above-described problems.  
15 In particular, in cosmetic formulations skin-friendly preparations can thereby be obtained providing a coloured cosmetic formulation which is highly safe to the skin, has sufficient high gel strength, good dispersion of the pigment, is good at spreading and application feel and has an anti-  
20 crinkle effect and a moisture-retaining effect.

Accordingly, the present invention relates to a dye-stuff based on platelet-shaped substances optionally coated with one or more metal oxides, characterized in that it contains a chiral iridescent liquid crystalline medium; in particular  
25 to such a colourant wherein

- a) the chiral iridescent liquid crystalline medium is linked to the surface of the platelet-shaped substrate,
- b) the chiral iridescent liquid crystalline medium is an admixture of at least one chiral component and at  
30 least one non-chiral component,

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- c) at least one chiral component is a compound of the formula I



wherein

- 5  $R^1$  is  $R^*$  or an alkyl radical or an alkenyl radical with up to 18 C atoms optionally substituted by CN or at least one halogen atom, wherein one or two non-adjacent  $CH_2$  groups of these radicals can also be replaced by -O-, -CO-, -O-CO- and/or  
10 -CO-O-,

$A^1$  and

$A^2$  are in each case independently of one another

- 15 a) a 1,4-cyclohexylene group, wherein one or two non-adjacent  $CH_2$  groups can also be replaced by -O- and/or -S- and/or which can be substituted in the 1-position by a CN- or  $CH_3$ -group,
- b) a 1,4-cyclohexenylene, a piperidine-1,4-diyl or 1,4-bicyclo[2,2,2]octylene group, or
- 20 c) a 1,4-phenylene group optionally substituted by one or two F-atoms or one or two CN- or one or two  $CH_3$ -groups, wherein at least one CH group can also be replaced by N,

- 25  $Z^1$  is -CO-O-, -O-CO-, - $CH_2CH_2$ -, -CHCN- $CH_2$ -, - $CH_2$ -CHCN-, CH=CH-, -O $CH_2$ -, - $CH_2$ O-, -CH=N-, -N=CH-, -NO=N-, -N=NO- or a single bond,

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m is 0, 1, 2 or 3, and

R\* is a chiral radical imparting optical activity to the compound of the formula I,

or a chiral steroid ester of the formula II

5

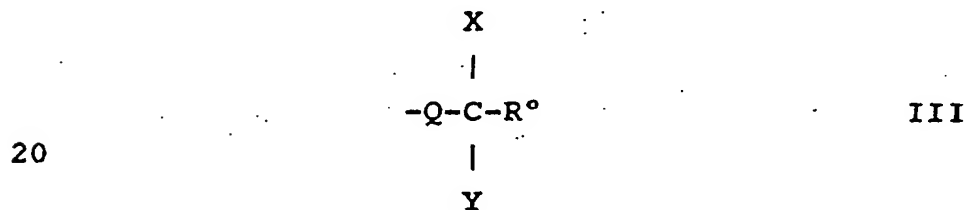


wherein

10 R<sup>3</sup> is a normal or branched alkyl or alkenyl radical with up to 16 C atoms wherein one CH<sub>2</sub> group may be replaced by -O-, -O-CO- or -CO-O-, and

15 Ster denotes a saturated or unsaturated gonan-3-yl group being optionally substituted by up to 6 normal or branched alkyl residues with 1 to 10 C atoms.

d) R\* is a chiral radical of the formula III



- 6 -

wherein

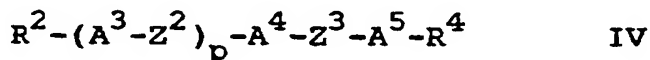
Q is a single bond or an alkylene group with 1-8  
C atoms, wherein one or two non-adjacent CH<sub>2</sub>  
groups can be replaced by -CH(CN)-, -CH(F)-,  
5 -CH(Cl)-, -O-, -S-, -CO-O- or O-CO

X is H or CH<sub>3</sub>

Y is F, Cl, Br, CN, CF<sub>3</sub> or CH<sub>3</sub> in the case that  
X is H

R° is an alkyl radical being different from X with up  
10 to 14 C atoms, wherein one or two non-adjacent  
CH<sub>2</sub> groups may be replaced by -O-, -CO-O- or -O-CO-.

e) at least one non-chiral compound is a compound of the  
formula IV



15 wherein

R<sup>2</sup> and R<sup>4</sup> in each case independently of one another  
are an alkyl radical or an alkenyl radical  
each with up to 18 C atoms optionally sub-  
stituted by CN or at least one halogen atom,  
20 wherein one or two non adjacent CH<sub>2</sub> groups  
of these radicals can also be replaced by  
-O-, -CO-, -O-CO- and/or -CO-O-, one of  
R<sup>2</sup> and R<sup>4</sup> may also be CN or halogen,



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$A^3$ ,  $A^4$   
and  $A^5$

are in each case independently of one another

5

a) a 1,4-cyclohexylene group, wherein one or two non-adjacent  $\text{CH}_2$  groups can also be replaced by -O- and/or -S- and/or which can be substituted in the 1-position by a  $\text{CH}_3$ - or CN-group,

10

b) a 1,4-cyclohexenylene, a piperidine-1,4-diyl or 1,4-bicyclo[2,2,2]octylene group, or

c) a 1,4-phenylene group optionally substituted by one or two F atoms or one or two  $\text{CH}_3$ - or one or two CN groups

15

$Z^2$  and  $Z^3$  are each -CO-O-, -O-CO-,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CHCH}-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CHCN}-$ ,  $-\text{CH}=\text{CH}-$ ,  $-\text{OCH}_2-$ ,  $-\text{CH}_2\text{O}-$ ,  $-\text{CH}=\text{N}-$ ,  $-\text{N}=\text{CH}-$ ,  $-\text{NO}=\text{N}-$ ,  $-\text{N}=\text{NO}-$  or a single bond, and

p is 0, 1 or 2,

f) the platelet-shaped substrate is mica,

20

g) the mica is coated by one or more metal oxides, and

h) the metal oxide is at least one group II, III, IV, V or VI metal oxide in an amount of 1 to 60 % by weight.

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Furthermore, the invention relates to  
a coloured lacquer composition,  
a coloured paint composition,  
a coloured fiber composition,  
5 a coloured glass composition,  
a coloured cosmetic composition and  
a coloured printing ink composition, wherein the colourant  
is based on platelet-shaped substances optionally coated  
with one or more metal oxides which is coated with a chiral  
10 iridescent liquid crystalline medium.

Preferred as the platelet-shaped substances used in the  
present invention are such having  $1.0 \times 10^{-5}$  mol/g or  
more of acidic points with acid strength  $H_o$  of -1.2 or  
less, and, for example, kaolin, bentonite, sericite, mica  
15 and other may be mentioned. Especially preferred are sericite,  
mica and other.

Particularly preferred platelet-shaped substances are mica  
coated with one or more metal oxides as, for example, titanium  
dioxide, iron oxide, chromium oxide, bismuth oxide. Particularly  
20 preferred are pearl lustre pigments distributed by E. Merck,  
Darmstadt, FRG, under the tradename Iriodin®.

Particularly preferred are mica pigments coated with  
dark coloured for example black or dark blue oxide layers  
which serve to enhance the colour of the chiral iridescent  
25 liquid crystal.

Preferably a hydrophobic layer is applied to the platelet-  
shaped substances before admixing them with the chiral iri-  
descent liquid crystalline media.

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The colourant according to the invention contains 0.1-50 % by weight, preferably 0.5-10 %, of the platelet shaped substances and 50 %-99.9 % by weight, preferably 90 %-99.5 % of the chiral iridescent liquid crystal medium.

- 5 The platelet shaped substance can be treated, for example, with dialkylphosphoric acid as in the case of mica described in Japanese Patent Application JP 63 238 011, with mono-alkoxytitanates as in the case of mica described in EP-03 06 056 or with silylating agents as in the case of  
10 mica described in EP-02 68 918.

Alternatively the platelet shaped substance may be treated with a Werner type surface active transition metal complex such as stearato chromic chlorid as described in Advances in Chemistry Series, Volume 23 (1959) pp 338-346.

- 15 Alternatively the platelet shaped substance may be treated with an active silicone derivative such as poly hydrogen methyl siloxane to obtain a hydrophobic surface.

- There are two important types of liquid crystal phases; the smectic mesophase in which the long range ordering is  
20 of a substantially lamellar type and the nematic mesophase in which the ordering is substantially linear, i.e. the molecules tend to line up with the long axes of the molecules parallel.

- Included sometimes as a subclass of the nematic mesophase and sometimes classified as a separate mesophase is the  
25 cholesteric mesophase. The latter has a helical long range order imposed upon the linear order of the nematic mesophase. Compounds displaying a cholesteric mesophase

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are optically active (chiral) and the pitch of the helical twist is determined by the nature and extent of the optical activity. The pitch of the helical twist may be such that thin films of the cholesteric phase reflect  
5 visible light, resulting in the observation of bright colours.

The chiral compounds of the formula I and the chiral steroid esters of the formula II because of their molecular shape and optical activity induce a cholesteric mesophase  
10 (hereinafter designated Ch) to the liquid crystalline composition containing the compounds of the formula IV which possess a nematic mesophase. As a result of these properties, the colourants according to the invention have not only a high refractive index and high gloss but also a very good  
15 skin feeling and an anti-crinkle effect.

The compounds of the formulae I, II and IV used according to the invention are known per se and have also already been proposed as components for liquid crystalline compositions which can be applied in electro-optical display devices  
20 or in temperature indicating devices. Processes for their preparation are described, for example, by R. Steinsträsser, Z. Naturforsch. 27b, 774 (1972), German Patent Application 2240864, U.S. Patent 4,136,053 or the British Patent Applications 8800800, 8800801 and 88 11 374, in "Flüssige  
25 Kristalle in Tabellen" Vol. I and II (liquid crystals in tables), VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1974 u. 1984, and other publications quoted in the literature mentioned above.

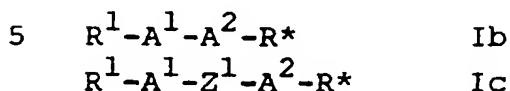
Above and below  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ ,  $R^*$ ,  $R^0$ ,  $A^1$ ,  $A^2$ ,  $A^3$ ,  $A^5$ ,  
30  $Z^1$ ,  $Z^2$ ,  $Z^3$ , Q, X, Y, m and p have the meaning given, unless expressly indicated otherwise.

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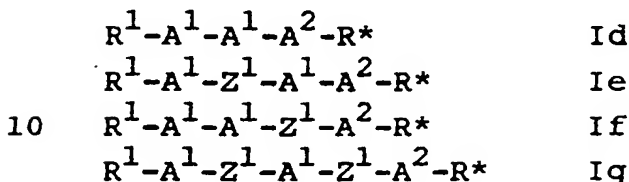
The compounds of the formula I include preferred compounds with one ring of the sub-formula Ia



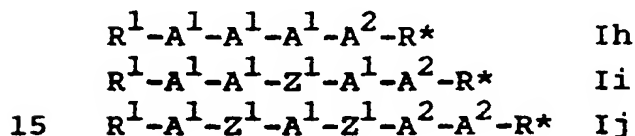
compounds with two rings of the sub-formulae Ib to Ic:



compounds with three rings of the sub-formulae Id to Ig



and compounds with four rings of the sub-formulae Ih to Ij



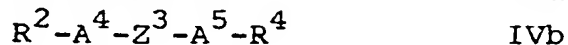
Above and below  $R^1$  denotes preferably alkyl or alkoxy.

In the compounds of the formulae I and Ia to Ij  $A^1$  and  $A^2$  preferably denote a 1,4-phenylene, group optionally substituted by a halogen atom, preferably by fluorine, or a pyrimidine-2,5-diyl group or a 1,4-cyclohexylene group.

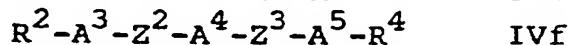
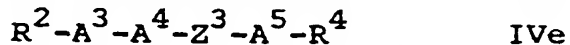
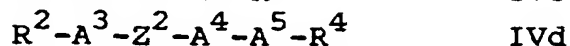
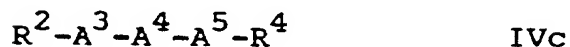
The compounds of the sub-formulae Ia, Ib and Ic are particularly preferred, in particular those compounds of the formula Ia wherein  $R^1$  is  $R^*$ .

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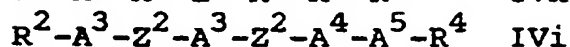
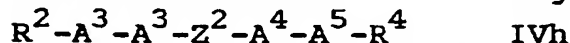
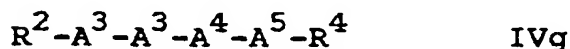
The achiral compounds of the formula IV include preferred compounds with two rings of the sub-formulae IVa to IVb



5 compounds with three rings of the sub-formulae IVc to IVf



10 and compounds with four rings of the sub-formulae IVg to IVi



15 In the compounds of the formulae IVa to IVi the rings  $A^3$ ,  $A^4$  and  $A^5$  have the same preferred meaning as given for  $A^1$  and  $A^2$  for the compounds of the formula I.

Above and below  $R^1$ ,  $R^2$  and  $R^4$  each preferably denote alkyl with preferably 1 to 13 C atoms, particularly 3 to 12 C atoms, wherein one or the two  $CH_2$  groups may be replaced  
20 by -O- or -CO-.

Preferably only one  $CH_2$  group is replaced, particularly preferred by -O-.

If  $R^1$ ,  $R^2$  and  $R^4$  each are an alkyl radical wherein one ("alkoxy" or "oxaalkyl") or two ("alkoxyalkoxy" or  
25 "dioxalkyl") nonadjacent  $CH_2$  groups may be replaced by -O-, these radicals can be straight-chained or branched.

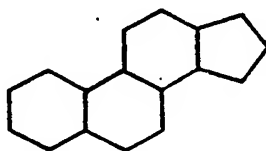
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Preferably, they are straight-chained and have 2, 3, 4, 5, 6, 7, 8, 9 or 10 C atoms and are accordingly preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, ethoxy, propoxy, butoxy, pentyloxy, hexyl-  
5 oxy, heptyloxy, nonyloxy, decyloxy, also methyl, undecyl, dodecyl, tridecyl, tetradecyl, methoxy, undecyloxy, dodecyloxy, tridecyloxy or tetradecyloxy.

Oxaalkyl is preferably straight-chained 2-oxapropyl (= methoxymethyl), 2-(=ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl),  
10 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl, 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl, 1,3-dioxabutyl (= methoxymethoxy);  
1,3-, 1,4-, 2,4-dioxapentyl, 1,3-, 1,4-, 1,5-, 2,4-, 2,5-  
15 or 3,5-dioxahexyl, 1,3-, 1,4-, 1,5-, 1,6-, 2,4-, 2,5-, 2,6-, 3,5-, 3,6- or 4,6-dioxahexyl.

The chiral steroid esters of the formula II used according the invention are also known per se, for example from Flüssigkristalle in Tabellen, VEB Deutscher Verlag für Grundstoff-  
20 industrie, Leipzig Vol. I 1974 and Vol. II, 1984.

In the compounds of the formula II Ster denotes a saturated or unsaturated gonan-3-yl group of the formula



being preferably substituted in the 5-, 10-, 13- and/or 17-position by normal or branched alkyl radicals with  
25 up to 10 C-atoms.

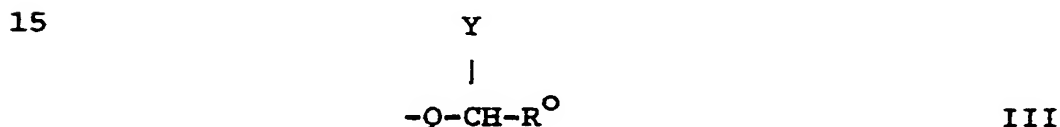
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The compounds of the formula II wherein Ster denotes a cholesterin-3-yl group are preferred.

Furthermore preferred are those compounds of the formula II wherein Ster denotes a cholestan-3-yl group, a cholest-2-en-3-yl group, a sitosterin-3-yl group, an 17-alkylan-drostan-3-yl group, an 17-alkylandrosten-3-yl group or an estron-3-yl group.

The residue  $R^3$  of the formula II preferably is an alkyl group with 1 to 13, preferably 2 to 10 C atoms.

10 The invention thus relates preferably to dye-stuffs based on platelet-shaped substances containing a chiral iridescent liquid crystalline medium comprising compounds of the formula I, in particular compounds of the formula I wherein  $R^*$  is a chiral radical of the formula III



wherein

Y denotes preferably  $CH_3$ , Cl, CN or F

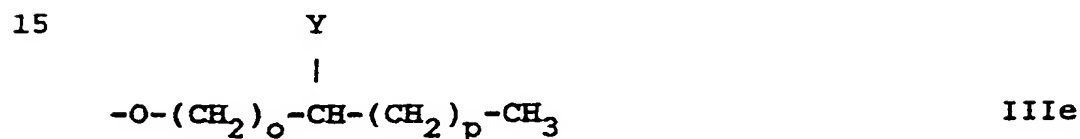
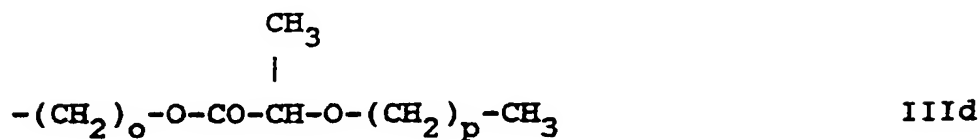
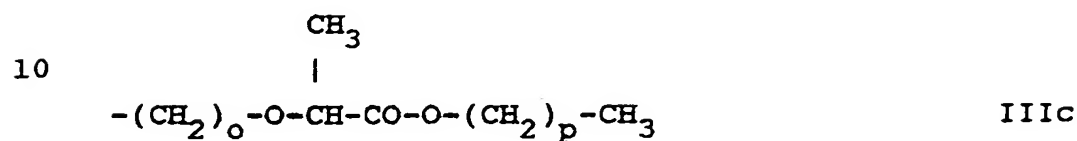
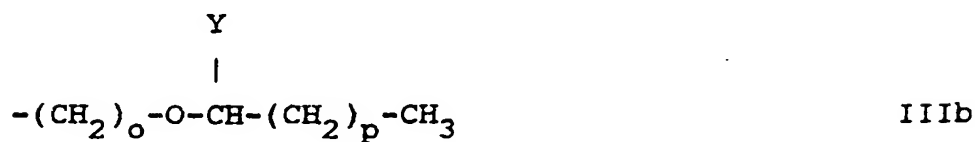
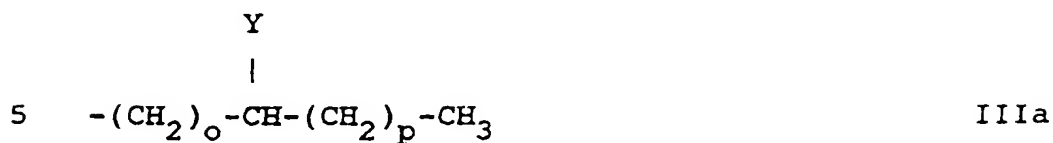
20 Q denotes preferably an alkylene residue with up to 7 C atoms wherein one  $CH_2$  group may be replaced by -O-, -CO-O- or -O-CO-, or a single bond,

25  $R^O$  denotes preferably an alkyl radical with 2 to 7 C atoms wherein one  $CH_2$  group may be replaced by -O-, -CO-O- or -O-CO-.

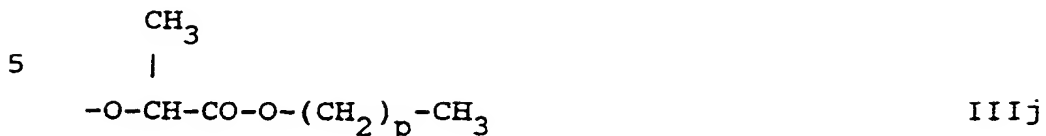
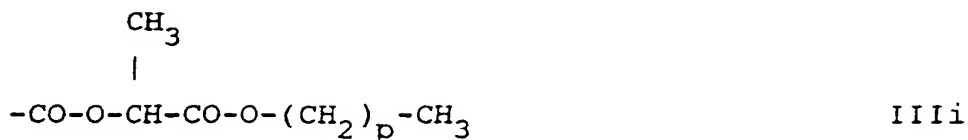


- 15 -

Preferred chiral groups of the formula III are those of the sub-formulae IIIa to IIIk:



- 16 -



- 10 In the groups of the formulae IIIa to IIIk o and p each are 1 to 6.

Particularly preferred are those compounds of the formula I wherein the residue R\* denotes a chiral group of the subformulae IIa, IIc, IId, IIg, IIIi or IIIk.

- 15 The chiral iridescent liquid crystalline phases formed by the compounds of the formulae I, II and IV preferably contain at least one, more preferred two or more, non-chiral compounds of the formula IV and at least one, preferably two, three or more, chiral esters of the formula I or II.
- 20 Said coloured liquid crystalline phases contain about 20 %-90 %, preferably 35 %-80 %, of one or more compounds of the formula I or II and about 10 %-80 %, preferably 20 %-65 %, of one or more compounds of the formula IV. In these chiral iridescent liquid crystalline phases the amount of the
- 25 compounds of the formula I or II and the amount of the compounds of the formula IV add up to 100 %.

The clearing point of these chiral iridescent liquid crystalline phases (Ch-I) lies preferably between 37 ° and 100 °C, particularly preferred between 50 °C and 90 °C.

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The chiral iridescent liquid crystalline phases used in the present invention are prepared in a manner which is customary per se. As a rule, the components are dissolved in one another, preferably at elevated temperature.

- 5 Because of the good gloss and the low weight of the inventive colourant, only relatively small amounts thereof are required in decorative compositions. Although the absolute amount depends on the nature of the formulation and the desired colour effect, as a rule about 1 %-50 %, by  
10 weight of the colourant preferably 5 %-20 % are employed.

The chiral iridescent liquid crystalline phases may be micro-encapsulated after admixing to platelet shaped substances.

- The microencapsulated chiral iridescent liquid crystalline phases are prepared in a manner which is customary per se  
15 (For example U.S. Patent 2,800,457).

The colourants according to the invention can be employed in decorative formulation for technical or cosmetic applications preferably for cosmetic applications.

- Vehicles used for the cosmetic formulations according to  
20 the invention are the substances customary for, for example, lipsticks, grease sticks, creams, powders and other cosmetics. These are known to the expert or are to be found in standard works, such as, for example, H. Janistyn, Handbuch der Kosmetika and Riechstoffe (Handbook of Cos-  
25 metics and Perfumes), Hüthig Verlag Heidelberg. Preferred vehicles are, for example, water based binders like polyvinyl alcohols or polyurethanes.

- Preferred vehicles for use in formulations are those which contain at most small amounts of volatile and  
30 low molecular weight organic compounds and solvents.

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The formulations according to the invention contain as colouring constituents in each case at least one of the abovementioned dye-stuffs based on platelet-shaped substances which are coated with chiral iridescent liquid crystalline media formed by the compounds of the formulae I or II and the compounds of the formula IV.

Very attractive colour effects are achieved. The present invention therefore provides very advantageous coloured compositions with very attractive colour effects and a very pleasant skin feeling.

The following examples are intended to illustrate the invention without limiting it. Percentages above and below are percentages by weight. All the temperatures are given in degrees Centigrade. The symbols are furthermore as follows: Cr: crystalline solid state, S: smectic phase (the index characterizes the phase type), N: nematic phase, Ch: cholesteric phase, I: isotropic phase. The figure between two symbols indicates the transition temperature.

#### Example 1

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	49.3 %
	p-pentylphenyl-p-hexyloxybenzoate	24.7 %
25	cholesteryl nonanoate	11.7 %
	cholesteryl valerate	7.4 %
	cholesteryl propionate	6.9 %

exhibits a bright, red colour and Ch 52.3 ° I

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## Example 3

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	44.5 %
5	p-pentylphenyl-p-hexyloxybenzoate	22.2 %
	cholesteryl nonanoate	15.0 %
	cholesteryl valerate	9.5 %
	cholesteryl propionate	8.8 %

exhibits a bright, green colour and Ch 53.9 ° I

## 10 Example 4

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	41.0 %
	p-pentylphenyl-p-hexyloxybenzoate	20.5 %
15	cholesteryl nonanoate	17.3 %
	cholesteryl valerate	11.0 %
	cholesteryl propionate	10.2 %

exhibits a bright, blue colour and Ch 55.6 ° I

## Example 5

20 A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	40.0 %
	p-pentylphenyl-p-hexyloxybenzoate	20.0 %
	cholesteryl nonanoate	18.0 %
25	cholesteryl valerate	11.1 %
	cholesteryl propionate	10.6 %

exhibits a bright, blue colour and Ch 56 ° I

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## Example 5

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	40.0 %
5	p-pentylphenyl-p-hexyloxybenzoate	20.0 %
	cholesteryl nonanoate	18.0 %
	cholesteryl valerate	11.1 %
	cholesteryl propionate	10.6 %

exhibits a bright, blue colour and Ch 56 ° I

## 10 Example 6

A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	38.0 %
	p-pentylphenyl-p-hexyloxybenzoate	19.0 %
15	cholesteryl nonanoate	19.3 %
	cholesteryl valerate	12.3 %
	cholesteryl propionate	11.4 %

exhibits a bright, purple colour and Ch 56.8 ° I

## Example 7

20 A cholesteric liquid crystalline mixture is formulated containing the following liquid crystalline components

	p-pentylphenyl-p-methoxybenzoate	18.0 %
	p-pentylphenyl-p-hexyloxybenzoate	16.0 %
	p-pentylphenyl-p-octyloxybenzoate	16.0 %
25	cholesteryl valerate	25.0 %
	cholesteryl nonanoate	25.0 %

exhibits a bright colour and Ch 57.6 ° I.

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The cholesteric liquid crystalline mixtures of the examples 1 to 7 are admixed to surface-modified (as described in Example 8) mica pigments to achieve decorative compositions with attractive coloured effects, pleasant skin feeling and anti-crinkle effect.

#### Example 8

Application of a thermochromic liquid crystalline medium to a mica pigment.

A solution of Edoran® (a solution of tetrachloro- $\mu$ -hydroxo- $\mu$ -stearatodichromo complex, which is available from Mitsubishi Gas Chemical Co. Limited, Tokyo, Japan) at a concentration of 3 % solids in distilled water is added to the mica pigment Black Pearl TM (Particle Size < 15  $\mu$ m/available from E. Merck, 6100 Darmstadt, FRG). Sufficient of the solution is added to provide a mobile slurry, which is stirred at room temperature for 30 minutes. After this period, the suspension is filtered on a Buchner funnel, rinsed once with water and dried in a vacuum oven at 40 °C overnight. The treated mica is mixed into the chiral liquid crystal mixture of example 3 at a concentration of 1 % by weight to provide a bright iridescent colourant. On emulsification in an aqueous phase prior to microencapsulation, or on mixing into a Carbopol gel, no migration of mica to the aqueous phase is observed.

Analogously the chiral nematic liquid crystal mixtures of the Examples 2 to 7 are applied to Black Pearl TM.

Analogously the chiral nematic liquid crystal mixtures of the Examples 1 to 7 are applied to the following platelet shaped substrates:

Mica M (available from E. Merck, Darmstadt, FRG)  
Mica MS (silanized Mica M)  
Silk Mica (available from Rona Pearl Bayonne, USA, Art. 17176).

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## Example 9

## Decorative cosmetic composition formulation

A 0.25 % by weight solution of Carbopol 940 (a water soluble copolymer of acrylic acid crosslinked with a polyalkenylpoly-  
5 ether, which is available from BF Goodrich Co, Cleveland, Ohio) in water is neutralised to pH 7.0 by careful addition of sodium hydroxide solution. A clear highly viscous gel is formed. By use of a nozzle, strands of colourant (of example 8) are in-  
10 jected into the gel to obtain an attractive cosmetic formulation having an iridescent colour effect in the bulk sample, and a pleasant smooth feeling when applied to the skin.

## Example 10

## Printing Ink Composition Formulation

The colourant of example 8 is emulsified into an aqueous  
15 solution of gelatin, and microencapsulated in gelatin-gum acacia coacervate according to the process of USP 2800457 example 2. The capsules are hardened by the process of USP 2800457 example 1. A slurry of microcapsules of mean diameter 18  $\mu$ m is obtained, and added to an aqueous solution  
20 of polyvinyl alcohol (PVA) to obtain a viscous suspension containing 8 % PVA and 20 % liquid crystal. The suspension is applied by screenprinting to a plain board, to give a bright iridescent colour effect without a separate black layer being required.

## 25 Example 11

A blue colourant is obtained by substituting a composition of example 5 for the liquid crystal in example 8. The colour-  
ant is incorporated into a mascara formulation according to UK Patent Application GB 89 10803.9 example 9 and provides  
30 enhanced colour brightness and contrast over that composition.



### Example 12

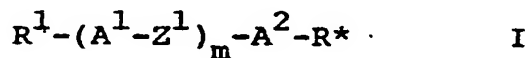
A mixture was made of TCP1005 (50 g), a thermochromic ink formulation commercially available from Merck Ltd., TCJ1005 (50 g), also a thermochromic ink commercially available from Merck Ltd., and lamellar molybdenum sulphide (2 g), from E. Merck catalogue number 12257. The mixture was agitated by means of an electric paddle stirrer until it was completely homogeneous. The resulting composition was coated onto a blackened card and air dried. The final coating gave an attractive thermochromic effect with a silver grey to matt black flop effect.

### Example 13

The procedure of Example 12 was followed, but the molybdenum sulphide was omitted, and an aluminium flake pigment, BASF type EM-21-3157 was used in its place. Prior to use of the pigment, it was freed of oily material by washing twice with five weights of tetrahydrofuran, and dried at 40 degrees C for 24 hours under vacuum. The resulting coating gave a spectacular flop effect, with metallic specular reflection close to normal incidence giving way to a thermochromic colour play at glancing angles.

## Claims

1. A colourant based on platelet-shaped substances optionally coated with one or more metal oxides, characterized in that it contains a chiral iridescent liquid crystalline medium.
2. A colourant according to Claim 1, characterized in that medium is linked to the surface of the platelet-shaped substrate.
3. A colourant according to Claim 1 or 2, characterized in that the iridescent liquid crystalline medium is an admixture of at least one chiral component and at least one non-chiral component.
4. A colourant according to Claim 3, characterized in that at least one chiral component is a compound of the formula I



wherein

$R^1$  is  $R^*$  or an alkyl radical or an alkenyl radical with up to 18 C atoms optionally substituted by CN or at least one halogen atom, wherein one or two

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non-adjacent  $\text{CH}_2$  groups of this radicals can also be replaced by -O-, -CO-, -O-CO- and/or -CO-O-,

$\text{A}^1$  and

5  $\text{A}^2$  are in each case independently of one another

10 a) a 1,4-cyclohexylene group, wherein one or two non-adjacent  $\text{CH}_2$  groups can also be replaced by -O- and/or -S- and/or which can be substituted in the 1-position by a CN- or  $\text{CH}_3$ -group,

b) a 1,4-cyclohexenylene, a piperidine-1,4-diyl or 1,4-bicyclo[2,2,2]octylene group, or

15 c) a 1,4-phenylene group optionally substituted by one or two F-atoms or one or two CN- or one or two  $\text{CH}_3$ -groups, wherein at least one CH group can also be replaced by N,

$\text{Z}^1$  is -CO-O-, -O-CO-,  $-\text{CH}_2\text{CH}_2-$ ,  $-\text{CHCN}-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CHCN}-$ ,  $\text{CH}=\text{CH}-$ ,  $-\text{OCH}_2-$ ,  $-\text{CH}_2\text{O}-$ ,  $-\text{CH}=\text{N}-$ ,  $-\text{N}=\text{CH}-$ ,  $-\text{NO}=\text{N}$ ,  $-\text{N}=\text{NO}-$  or a single bond,

20 m is 1, 2 or 3, and

$\text{R}^*$  is a chiral radical imparting optical activity to the compound of the formel I, or a chiral steroid ester of the formula II

O

25

$\text{Ster-O-C-CH}_2-\text{R}^3$

II

wherein

$R^3$  is a normal or branched alkyl or alkenyl radical with up to 16 C atoms wherein one  $CH_2$  group may be replaced by -O-, -O-CO- or -CO-O-, and

Ster denotes a saturate or unsaturated gonan-3-yl group being optionally substituted by up to 6 normal or branched alkyl radicals with 1 to 10 C atoms.

- 10 5. A colourant according to Claim 4, characterized in that  $R^*$  is a chiral radical of the formula III



wherein

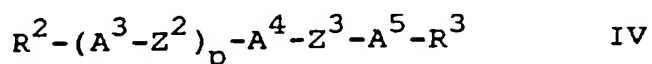
20 Q is a single bond or an alkylene group with 1-8 C atoms, wherein one or two non-adjacent  $CH_2$  groups can be replaced by -CH(CN)-, -CH(F)-, -CH(Cl)-, -O-, -S-, -CO-O- or O-CO

X is H or  $CH_3$

Y is F, Cl, Br, CN or  $CF_3$

R° is an alkyl residue being different from X with up to 14 C atoms, wherein one or two non-adjacent CH<sub>2</sub> groups may be replaced by -O-, -CO-O- or -O-CO-.

6. A colourant according to at least one of the claims 3 and 5, characterized in that at least one non-chiral compound is a compound of the formula IV



R<sup>2</sup> and R<sup>3</sup> in each case independently of one another are an alkyl radical or an alkenyl radical each with up to 18 C atoms optionally substituted by CN or at least one halogen atom, wherein one or two non adjacent CH<sub>2</sub> groups of these radicals can also be replaced by -O-, -CO-, -O-CO- and/or -CO-O-, one of R<sup>2</sup> and R<sup>3</sup> may also be CN or halogen,

A<sup>3</sup>, A<sup>4</sup>  
and A<sup>5</sup> are in each case independently of one another

- a) a 1,4-cyclohexylene group, wherein one or two non-adjacent CH<sub>2</sub> groups can also be replaced by -O- and/or -S- and/or which can be substituted in the 1-position by a CH<sub>3</sub>- or CN-group,
- b) a 1,4-cyclohexenylene, a piperidine-1,4-diyl or 1,4-bicyclo[2,2,2]octylene group, or

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c) a 1,4-phenylene group optionally substituted by one or two F atoms or one or two CH<sub>3</sub>- or one or two CN groups

5           Z<sup>2</sup> and Z<sup>3</sup> are each -CO-O-, -O-CO-, -CH<sub>2</sub>CH<sub>2</sub>-, -CHCH-CH<sub>2</sub>-,  
              -CH<sub>2</sub>-CHCN-, -CH=CH-, -OCH<sub>2</sub>-, -CH<sub>2</sub>O-, -CH=N-,  
              -N=CH-, -NO=N, -N=NO- or a single bond, and

p           is 0, 1 or 2.

- 10       7. A colourant according to at least one of the Claims 1 to 6, characterized in that the platelet-shaped substrate is mica.
8. A colourant according to Claim 7 based on a platelet-shaped substance which is coated by one or more metal oxides.
- 15       9. A colourant according to Claim 7 or 8 which is coated with at least one group II, III, IV, V or VI metal oxide in an amount of 1 to 60 % by weight.
10. A colourant lacquer composition, wherein the colourant is a colourant of claim 1.
- 20       11. A colourant paint composition, wherein the colourant is a colourant of claim 1.
12. A colourant plastic composition, wherein the colourant is a colourant of claim 1.

13. A dyed fiber composition, wherein the colourant is a colourant of claim 1.
14. A dyed glass composition, wherein the colourant is a colourant of claim 1.
- 5 15. A dyed cosmetic composition, wherein the colourant is a colourant of claim 1.
16. A dyed printing ink composition, wherein the colourant is a colourant of claim 1.
- 10 17. A hair colouring agent, wherein the colourant is a dye-stuff of claim 1.



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